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On the Adsorption of Strong Electrolytes.

By

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Of adsorption of strong electrolytes by solid substances, only few facts are definitely known, as may be seen from the following quotation from H. Freundlich's excellent work "Kapillarchemie."[1]

"Es ist nicht verwunderlich, dass über die Adsorption stark dissoziierter Stoffe an festen Grenzflächen zur Zeit wenig Sicheres zu sagen ist. Man hat es ja in der Lösung mit verwickelten Gleichgewichten zwischen mehrere Stoffen zu tun, muss also eine Adsorption aus einem Gemisch mehrerer Stoffe in Rücksicht ziehen; dazu kommen noch kapllarelektrische Einflüsse. Die Angaben über die Adsorption von Salzen sind daher nochrecht widerspruchsvoll und schwer zu deuten.

"Allein schon die Frage nach dem Vorzeichen der Adsorption ist nicht eindeutig zu beantworten. Lagergren arbeitete mit Kohle und Kaolin als Adsorbentien in ziemlich konzentrierten (ca. 1-molar) Salzlösungen; er beobachtete eine sehr geringe, aber positive Adsorption bei den Nitraten des Natriums, Kaliums, Ammoniums und Baryums. Bei den Chloriden derselben Metalle (ausserdem noch bei Magnesium) war die Konzentration in der Lösung nach der Adsorption grösser als vorher: es war also eine negative Adsorption eingetreten; negativ adsorbiert wurde auch Bromammonium. Bei den Sulfaten war die Adsorption überhaupt gering, sie schien in einigen Fällen positiv, in anderen negativ zu sein..."

It has usually been assumed that the quantity of the solvent adsorbed by the adsorbent may be neglected, as the amount of the adsorbent used is small.[2] But in the case of strong electrolytes, since the adsorption is very slight, the negligence of that of water is not

1 p. 165.

2 Freundlich, *Loc. cit.* 166.

admissible and may have been the cause of irregularity ef adsorption in some cases.

Because of such a consideration the author has undertaken the study of the adsorption of some strong electrolytes by blood charcoal and the results so far obtained are here communicated.

The blood charcoal used was C. Kahlbaum's preparation. It was digested in dilute hydrochloric acid for a few days, then washed by decantation with hot distilled water once or twice a day for about two months, and finally washed on a filter and dried at about 120° to a constant weight. It was preserved in a desiccator over sulphuric acid. It was quite free from chloride, but when shaken with water, it gave traces of extract, which was quantitatively determined, as was necessary for the present method of experiment, as may be seen later.

The salts used were purified in the usual way by recrystallisation, except the potassium bromide and iodide (Pharm. Jap.) which was directly used.

The experiments were carried out in the following way: A small Erlenmeyer flask of about 50 cc. capacity with a paraffined cork stopper was weighed, some refined blood charcoal was put in it and the whole was weighed again. About 50 cc. of a salt solution of an approximately known concentration was added to the flask which was weighed again. The cork stopper was fastened to the neck of the flask with copper wire and was made perfectly water-tight by paraffin. The flask was made to rotate in a thermostat at 25·0° for at least two days, then let stand still in the same thermostat for a day. About 10 cc. of the clear solution was taken out by a pipette, with a glass tube attached, filled with refined cotton previously washed with the same solution, and transferred into a weighed wide glass tube, drawn up at both ends, a so-called duck-tube,[1] and weighed. It was evaporated over a very small flame to dryness and then heated in an air-bath at about 120° to a constant weight. About 10 cc. of the original solution was also taken in a weighed duck-tube and treated in the same way.

As the contents of the solution were thus estimated by direct weighing of the residue, it was necessary to estimate the extract from the blood charcoal, though it was very slight. For this purpose, blood charcoal was treated with distilled water in the same way as with solutions. As the result of 10 experiments, a residue of 0·0003 grm.

1 Ostuald-Luthur Physiko-chemische Messungen, 3 ed., p. 264.

was obtained for 10 cc. of water, snd therefore 0·0003 grm. was subtracted from the weight of the residue from a solution treated with blood charcoal, variations of the amount of charcoal used being disregarded as influential merely within the sphere of experimental error.

The method of calculation, being somewhat complicated, one case of potassium iodide will be given in detail, as illustration.

1. Solution before Adsorption.

	(1)	(2)
Solution taken in a duck-tube	11·109	11·097
Residue after drying up	1·6352	1·6342
Salt in 10 grm. of the solution	1·4720	1·4727
The same corrected for bouyancy in air	1·4724	1·4731
Mean:	1·4728	

2. Solution after Adsorption.

	(1)	(2)
Solution taken in a duck-tube	10·928	11·084
Residue after drying up	1·5732	1·5962
Residue from 10 grm. of the solution	1·4399	1·4400
Extract from blood charcoal	0·0003	0.0003
Salt in 10 grm. of the solution	1·4396	1·4397
The same corrected for bouyancy in air	1·4400	1·4401
Mean:	1·4401	

The results of such calculations are as follows:

TABLE I.

No.	Salt in grm. in 10 grm. solution					
	before adsorption.			after adsorption.		
	(1)	(2)	Mean	(1)	(2)	Mean
	Sodium chloride.					
1	0·5629	0·5629	0·5629	0·5639	0·5636	0·5638
2	0·5078	0·5081	0·5080	0·5080	0·5082	0·5081
3	0·3974	0·3979	0·3977	0·3978	0·3976	0·3977
4	0·3422	9·3418	0·3420	0·3422	0·3424	0·3423

No.	Salt in grm. in 10 grm. solution					
	before adsorption.			after adsorption.		
	(1)	(2)	Mena	(1)	(2)	Mean
			Sodium nitrate.			
1	0·8014	0·8013	0·8014	0·7913	0·7917	0·7915
2	0·6773	0·6763	0·6768	0·6660	0·6659	0·6660
3	0·5437	0·5433	0·5435	0·5331	0·5333	0·5332
4	0·4100	0·4108	0·4104	0·4020	0·4021	0·4021
			Sodium sulphate.			
1	0·8050	0·8052	0·8051	0·8132	0·8131	0·8132
2	0·6965	0·6967	0·6966	0·7026	0·7034	0·7030
3	0·5558	0·5561	0·5560	0·5607	0·5610	0·5609
4	0·4254	0·4252	0·4253	0·4288	0·4285	0·4287
			Potassium chloride.			
1	0·9150	0·9152	0·9151	0·9191	0·9197	0·9194
2	0·7332	0·7337	0·7335	0·7384	0·7382	0.7383
3	0·4538	0·4548	0·4543	0·4541	0·4537	0·4539
4	0·3647	0·3642	0·3645	0·3646	0·3640	0·3643
			Potassium bromide.			
1	1·0527	1·0528	1·0528	1·0437	1·0443	1·0440
2	0·7630	0·7628	0·7629	0·7557	0·7557	0·7557
3	0·5525	0·5533	0·5529	0·5453	0·5454	0·5454
			Potassium iodide.			
1	1·4724	1·4731	1·4728	1·4400	1·4401	1·4401
2	1·2901	1·2897	1·2899	1·2592	1·2599	1·2596
3	0·9912	0·9919	0·9916	0·9622	0·9629	0·9626
4	0·7583	0·7589	0·7586	0·7304	0·7304	0·7304
			Potassium nitrate.			
1	0·9499	0·9507	0·9503	0·9352	0·9360	0·9356
2	0·8003	0·8009	0·8006	0·7898	0·7892	0·7895
3	0·6499	0·6505	0·6502	0·6370	0·6376	0·6373
4	0·4952	0·4950	0·4951	0·4842	0·4834	0·4838

No.	Salt in grm. in 10 grm. solution					
	before adsorption.			after adsorption.		
	(1)	(2)	Mean	(1)	(2)	Mean
			Potassium sulphate.			
1	0·8204	0·8208	0·8206	0·8263	0·8265	0·8264
2	0·6838	0·6840	0·6839	0·6879	0·6879	0·6879
3	0·5596	0·5596	0·5596	0·5629	0·5627	0·5628
4	0·4285	0·4282	0·4283	0·4304	0·4306	0·4305

As seen from the table, sodium nitrate, potassium bromide, potassium iodide and potassium nitrate are positively adsorbed and sodium chloride, sodium sulphate and potassium sulphate are negatively adsorbed, apparently. As to the solution of potassium chloride, when concentration is comparatively high, it is positively adsorbed and when comparatively low, negatively adsorbed, apparently. These distinct forms of adsorption may easily be explained by the fact that the adsorption of the solute is in some cases greater than that of the solvent and in others it is less.

In order to determine the quantity of salt adsorbed, we must determine the total amount of the salt in the solution, before and after adsorption. The former is given in Table 2. The apparent density of the solution and its true weight, deduced by means of it, are also given in the same table for subsequent use.

TABLE 2.

No.	Density.	Solution taken.		Salt in 10 grm. (apparent) solution.	Salt in the solution taken.
		Apparent wght.	Corrected wght.		
			Sodium chloride		
1	1·0366	51·858	51·910	0·5629	2·9191
2	1·0328	51·630	51·682	0·5080	2·6228
3	1·0251	51·256	51·309	0·3977	2·0385
4	1·0208	51·025	51·077	0·3420	1·7450

No.	Density.	Solution taken.		Salt in 10 grm. (apparent) solution.	Salt in the solution taken.
		Apparent wght.	Corrected wght.		
		Sodium nitrate.			
1	1·0512	52·610	52·662	0·8014	4·2161
2	1·0421	52·146	52·198	0·6768	3·5292
3	1·0327	51·665	51·716	0·5435	2·8080
4	1·0242	51·275	51·326	0·4104	2·1043
		Sodium sulphate.			
1	1·0702	53·506	53·558	0·8051	4·3078
2	1·0603	53·028	53·080	0·6966	3·6938
3	1·0475	52·383	52·435	0·5560	2·9125
4	1·0354	51·698	51·750	0·4253	2·1985
		Potassium chloride.			
1	1·0553	52·654	52·707	0·9151	4·8184
2	1·0437	52·020	52·072	0·7335	3·8157
3	1·0250	51·253	51·306	0·4543	2·3284
4	1·0194	50·999	51·051	0·3645	1·8589
		Potassium bromide.			
1	1·0762	53·664	53·716	1·0528	5·6497
2	1·0534	52·504	52·556	0·7629	4·0055
3	1·0369	5·1781	51·833	0·5529	2·8630
		Potassium iodide.			
1	1·1149	55·689	55·740	1·4728	8·2019
2	1·0988	54·836	54·887	1·2899	7·0733
3	1·0733	53·626	53·678	0·9916	5·3176
4	1·0545	52·659	52.711	0·7586	3·9936
		Potassium nitrate.			
1	1·0563	52·868	52·920	0·9503	5·0240
2	1·0474	52·376	52·428	0·8006	4·1932
3	1·0374	51·883	51·935	0·6502	3·3734
4	1·0273	51·387	51·439	0·4951	2·5442

No.	Density.	Solution taken.		Salt in 10 grm. (apparent) solution.	Salt in the solution taken.
		Apparent wght.	Corrected wght.		
		Potassium sulphate.			
1	1·0638	53·108	53·161	0·8206	4·3580
2	1·0520	52·618	52·671	0·6839	3·5985
3	1·0419	52·049	52·102	0·5596	2·9124
4	1·0305	51·575	51·628	0·4283	2·2090

Since the amount of salt in a given quantity of solution has been determined, the total amount of salt remaining in solution after adsorption may easily be found, if the total amount of solution after adsorption or that of water in it be known. In order to obtain the amount of water remaining in solution after adsorption, that adsorbed by charcoal must be estimated, but as there is no direct means for its determination, the following procedure was taken. Some water was put in the bottom of a small glass vessel of desiccator form about 9 cm. high, a small glass basin with a given quantity of blood charcoal was placed over it and the cover was water-tightly sealed with *picetin*. The whole apparatus was completely dipped into a thermostat at 25·0° and the basin with charcoal was weighed at intervals of about a week, until it became constant in weight, being kept during the weighing between a pair of watch-glasses. This required about one month; and, as a mean of 5 determinations, it was ascertained that animal charcoal, treated as above stated, adsorbed water to 85 per cent of its weight. As the solutions used in the experiments were about 1 normal or less, it was assumed that the amount of water adsorbed by blood charcoal from solution does not much differ from that adsorbed from pure water.

The total amount of water in the solution after adsorption was obtained as the difference of the quantity of the solution taken and the quantities of the salt and of the water adsorbed by the charcoal. Then the total amount of the salt remaining in the solution after adsorption was found from the composition of the final solution and the total amount of water remaining in the solution. The results are given in Table 3.

TABLE 3.

No.	Blood charcoal.	Water adsorbed by charcoal.	Water in the solution after adsorption.	Salt in 10 grm. (app.) solution after adsorption.	In 10 grm. (corr.) solution after adsorption.		Total salt in the solution after adsorption.
					Salt.	Water.	
				Sodium chloride.			
1	1·505	1·275	47·716	0·5638	0·5632	9·437	2·8477
2	1·259	1·071	47·988	0·5081	0·5076	9·492	2·5662
3	1·568	1·335	47·935	0·3977	0·3973	9·603	1·9832
4	1·495	1·275	48·057	0·3423	0·3420	9·658	1·7017
				Sodium nitratc.			
1	1·304	1·109	47·337	0·7915	0·7907	9·209	4·0644
2	1·291	1·097	47·570	0·6660	0·6653	9·335	3·3903
3	1·412	1·200	47·708	0·5332	0·5327	9·467	2·6847
4	1·298	1·102	48·120	0·4021	0·4017	9·598	2·0139
				Sodium sulphate.			
1	1·365	1·160	48·090	0·8132	0·8124	9·198	4·2525
2	1·362	1·157	48·229	0·7030	0·7023	9·298	3·6429
3	1·458	1·240	48·282	0·5609	0·5604	9·440	2·8660
4	1·442	1·226	48·325	0·4287	0·4282	9·572	2·1617
				Potassium chloride.			
1	1·447	1·230	46·659	0·9194	0·9185	9·081	4·7191
2	1·596	1·357	46·899	0·7383	0·7376	9·268	3·7347
3	1·315	1·118	47·860	0·4539	0·4535	9·546	2·2735
4	1·386	1·179	48·019	0·3643	0·3638	9.636	1·8129
				Potassium bromide.			
1	1·463	1·244	46·822	1·0440	1·0430	8·967	5·4461
2	1·431	1·216	47·334	0·7557	0·7549	9·245	3·8651
2	1·545	1·313	47·657	0·5454	0·5448	9·455	2·7460
				Potassium iodide.			
1	1·573	1·337	46·201	1·4401	1·4388	8·561	7·7647
2	1·487	1·264	46·550	1·2596	1·2583	8·742	6·7003
3	1·491	1·267	47·093	0·9626	0·9613	9·039	5·0084
4	1·573	1·337	47·380	0·7304	0·7297	9·270	3·7296

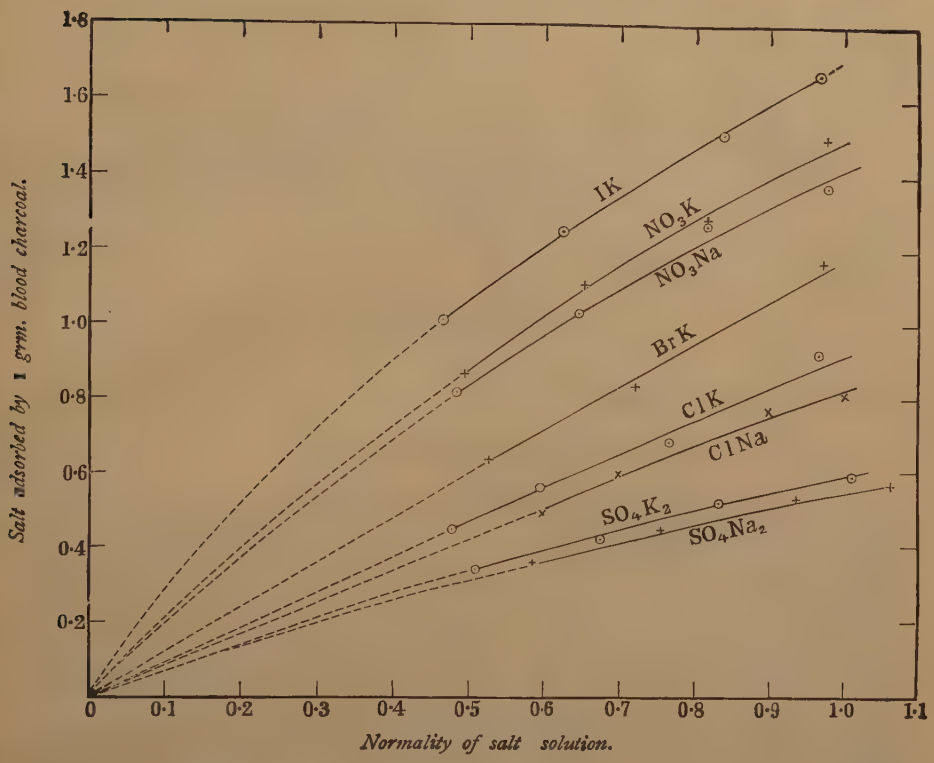
No.	Blood charcoal.	Water adsorbed by charcoal.	Water in the solution after adsorption.	Salt in 10 grm. (app.) solution after adsorption.	In 10 grm. (corr.) solution after adsorption.		Total salt in the solution after adsorption.
					Salt.	Water.	
			Potassium nitrate.				
1	1·334	1·142	46·754	0·9356	0·9347	9·065	4·8208
2	1·103	0·937	47·298	0·7895	0·7887	9·211	4·0499
3	1·296	1·102	47·460	0·6373	0·6367	9·363	3·2273
4	1·309	1·113	47·782	0·4838	0·4833	9·517	2·4294
			Potassium sulphate.				
1	1·360	1·156	47·647	0·8264	0·8256	9·174	4·2883
2	1·294	1·096	47·976	0·6879	0·6872	9·313	3·5401
3	1·277	1·089	48·100	0·5628	0·5622	9·438	2·8652
4	1·394	1·181	48·238	0·4305	0·4301	9·569	2·1681

Now, the total amount of salt, before and after adsorption, have been found and the quantity of salt adsorbed may easily be calculated. The normality of solution was obtained from its density before adsorption and its composition under the admissible assumption that the density does not change practically by adsorption. The results of calculation are represented in Table 4.

TABLE 4.

No.	Total salt in solution.		Salt adsorbed.	Blood charcoal.	Salt adsorbed by 1 grm. charcoal.		Normality of the solution.
	Before adsorption.	After adsorption.			grm.	Milligram equivalent.	
				Sodium chloride.			
1	2·9191	2·8477	0·0714	1·505	0·0474	0·81	0·998
2	2·6228	2·5662	0·0566	1·259	0·0449	0·77	0·896
3	2·0385	1·9832	0·0553	1·568	0·0353	0·60	0·697
4	1·7450	1·7017	0·0433	1·495	0·0290	0·49	0·597
				Sodium nitrate.			
1	4·2161	4·0644	0·1517	1·304	0·1517	1·37	0·978
2	3·5292	3·3903	0·1389	1·291	0·1389	1·27	0·816
3	2·8080	2·6847	0·1233	1·241	0·1233	1·03	0·647
4	2·1043	2·0139	0·0904	1·298	0·0904	0·82	0·484

No.	Total salt in solution.		Salt adsorbed.	Blood charcoal.	Salt adsorbed by		Normality of the solution.
	Before adsorption.	After adsorption.			grm.	Milligram equivalent.	
				Sodium sulphate.			
1	4·3078	4·2525	0·0553	1·365	0·0405	0·57	1·068
2	4·6938	3·6429	0·0509	1·362	0·0374	0·53	0·933
3	2·9125	2·8660	0·0465	1·458	0·0319	0·45	0·753
4	2·1985	2·1617	0·0368	1·442	0·0255	0·36	0·583
				Potassium chloride.			
1	4·8184	4·7191	0·0993	1·447	0·0686	0·92	0·966
2	3·8157	3·7347	0·0810	1·596	0·0508	0·68	0·765
3	2·3284	2·2735	0·0549	1·315	0·0418	0·56	0·562
4	1·8589	1·8129	0·0460	1·386	0·0332	0·45	0·479
				Potassium bromide.			
1	5·6497	5·4461	0·2036	1·463	0·1392	1·17	0·970
2	4·0055	3·8651	0·1404	1·431	0·0981	0·82	0·717
3	2·8630	2·7460	0·1170	1·545	0·0757	0·64	0·526
				Potassium iodide.			
1	8·2019	7·7647	0·4372	1·573	0·2779	1·67	0·967
2	7·0733	6·7003	0·3730	1·487	0·2508	1·51	0·833
3	5·3176	5·0084	0·3092	1·491	0·2074	1·25	0·622
4	3·9936	3·7296	0·2640	1·573	0·1678	1·01	0·464
				Potassinm nitrate.			
1	5·0240	4·8208	0·2032	1·344	0·1512	1·50	0·977
2	4·1932	4·0499	0·1433	1·103	0·1299	1·28	0·817
3	3·3734	3·2273	0·1461	1·296	0·1127	1·11	0·654
4	2·5442	2·4294	0·1148	1·309	0·0877	0·87	0·491
				Potassium sulphate.			
1	4·3580	4·2883	0·0697	1·360	0·0514	0·59	1·010
2	3·5985	3·5401	0·0584	1·294	0·0451	0·52	0·830
3	2·9124	2·8652	0·0472	1·277	0·0370	0·42	0·673
4	2·2090	2·1681	0·0409	1·394	0·0293	0·34	0·509



The relation between the normality of the solution and the quantity of the salt adsorbed in milligram-equivalents is graphically represented in Fig. 1.

From the figure it is seen that potassium salts are more adsorbep than the corresponding sodium salts, and this is a generally known fact. With salts of the same base, the degrees of adsorption are in the following order:

$$I > NO_3 > Br > Cl > SO_4.$$

The so-called Hofmeister's series of the precipitating power of anions for alkaline sols is as follows:

$$CNS < I < Br < NO_3 < Cl < C_2H_3O_2 < HPO_3 < SO_4.$$

Then W. Pauli, S. Posternak and R. Höber have found that the series is reversed for sols of acid reaction.[1]

The reverse of Hofmeister's series and the series have found for

1 *cf.* Cassuto, Die Kolloide Zustand der Materie, p. 96 (1913).

adsorption agree except in the case of bromide and nitrate which are reversed.

The following quotation from H. Bechhold's work will not be without interest in connection with the author's result.[1]

" Anorganische Salze erhöhen meist die Oberflächenspannung von Wasser, und zwar ergibt sich nach einer Tabelle von W. K. Röntgen und J. Schneider folgende Reihe für die Erhöhnng der Oberflächenspannung durch jodalkalien :

$$Na > K > Li > NH_4$$

bei den Anionen sämtlicher Alkalien :

$$CO_2 > SO_4 > Cl > NO_3 > J.$$

" In ähnlicher Reihenfolge wird durch Neutralsalze die Kompressibilität, die Löslichkeitsbeeinflussung und Zähigkeit des Wassers verändert. Aber die Beziehung ist noch weit ausgedehnter: die Neutralsalze können katalitische Wirkungen beschleunigen und verlangsamen: die Inversion des Rohrzuckers, die Esterverseifung, die Umwandlung von Azeton in Diazetonalkohol, und zwar ist die Wirkung in saurer Lösung meist umgekehrt wie die in alkalischer, worauf R. Höher hingewiesen hat. Im sauren Medium ist die Beschleunigung durch die Kationen :

$$Li > Na > K > Rb > Cs$$

im alkalischen Medium :

$$Cs > Rb > K > Na > Li$$

für die Anionen gilt in sauren Lösung die Reihe :

$$J > NO_3 > Br > Cl > CH_3CO_2 > SO_4$$

in alkalischer Lösung die umgekehrte."

As may be seen, the series of cations in acid solutions and that of anions in alkaline solutions are in perfect agreement with the author's series. Since the adsorption of salt is intimately connected with the precipitation of a sol and also with its influence on the surface tension of water, this agreement is not a mere accident.

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[1] Die Kolloide in Biologie und Medizin, p. 74 (1912). See also J. Traube, J. Phys. Chem., **14**, 452 (1910).

On the Equilibrium of a System of three Components where two Liquid-Phases co-exist.

By

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(Received October 7, 1915.)

The system of three components where two liquid-phases co-exist was studied by W. D. Bancroft[1] about twenty years ago. He pointed out that the Mass law could be applied to a case of equilibrium of such a system. In which case the exponential factors of the mathematical formula of mass law representing the equilibrium are neither necessarily nor usually integers.

"Let A and B be two non-miscible liquid, S the common solvent with which A and B are miscible in all proportions when taken singly, and let the amount of S remain constant, so that we are considering the amounts of A and B, namely x and y, which will dissolve simultaneously in a fixed amount of S. This, being a case of equilibrium, must come under the general equation of equiliblium,

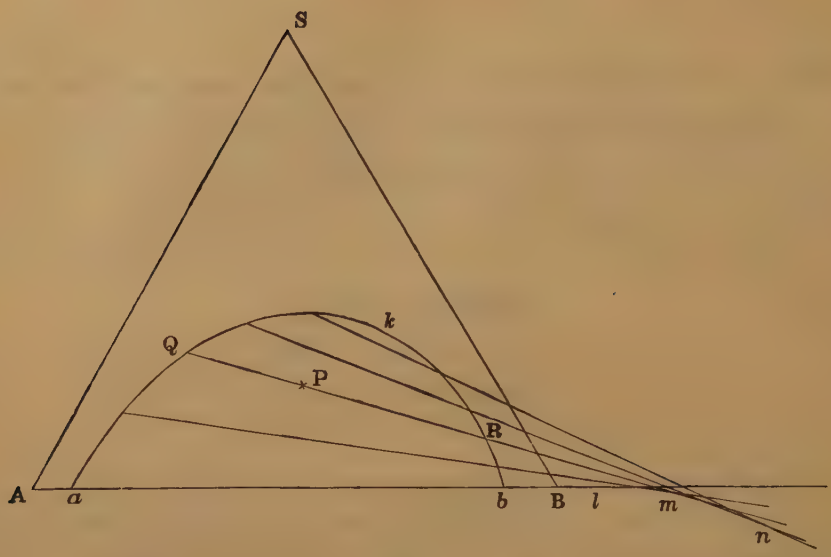
$$\frac{\delta F(x,y)}{\delta x}dx + \frac{\delta F(x,y)}{\delta y}dy = 0 \qquad (1)$$

where dx and dy denote the changes in the concentrations of A and B respectively. If it is assumed, in accordance with the Mass law, that the change in solubility is a function of the amounts of A and B already present,

$$\frac{\alpha}{x}dx + \frac{\beta}{y}dy = 0 \qquad (2)$$

or $$\alpha\, d\ln x + \beta\, d\ln y = 0$$

1 Physic. Rev., 3, 21, (1895); J. Chem. soc., Abst., 68, 157, (1995).



where α and β are proportionality factors. If these are constants, and $\alpha/\beta = n$, we get, after integration and clearing of logarithms,

$$x^n y = \text{Const.} \qquad (3)$$

"It is fouud, however, that in most cases the concentrations can not be given by one curve, but involve two, so that for one set of concentrations we have the relation

and for the other set
$$\left.\begin{aligned} x^{n_1} y &= C_1 \\ x^{n_2} y &= C_2 \end{aligned}\right\} \qquad (4)$$

The two sets of saturated solutions correspond with different conditions. Thus, in the chloroform-water-alcohol series, the one set of solutions is saturated in respect to chloroform and not in respect to water; the other set is saturated in respect to water and not in respect to chloroform."

In the present paper a further theoretical study of the equilibrium of such a system of three components is given. If the triangular coordinates be taken to express the three components system as usual, the compositions of two sets of the saturated solutions will be represented by the curve $a\,k\,b$ in the figure and ak is the saturated solutions of A with respect to B and $k\,b$ that of B with respect to A. Ac-

cording to Bancroft's consideration, if we take a definite amount of S, the above mentioned relation (4) must hold; but these relations can not be directly used in reference to the triangular co-ordinates here choosen, but must be transformed as follows:

$$\left.\begin{aligned} \frac{x^{n_1}y}{z^{n_1+1}} &= C_1(x+y+z)^{n_1+1} \\ \frac{x^{n_2}y}{z^{n_2+1}} &= C_2(x+y+z)^{n_2+1} \end{aligned}\right\} \qquad (5)$$

where $x+y+z = 1$. These equations correspond to the curves *ak* and *kb*. They do not, however, express the condition of equilibrium between two liquid-phases which might co-exist. It is evident that this condition is most important to determine the equilibrium of the system. If we take such a mixture as is represented by P in the figure, it will be separated in equilibrium into two liquid phases of the compositions represented by Q and R; and these two points evidently must be on the curves of equations (5).

Let the total number of mols in P be N, and A, B and S be in ratios of x_0, y_0 and z_0. Again let the total number of mols in the solutions Q and Z be n_a and n_b respectively, and the ratios of the three components in them respectively be x_a, y_a, z_a and x_b, y_b, z_b. Then we get the following relations

$$n_a x_a + n_b x_b : n_a y_a + n_b y_b : n_a z_a + n_b z_b = x_0 : y_0 : z_0,$$

or
$$\frac{n_a x_a + n_b x_b}{x_0} = \frac{n_a y_a + n_b y_b}{y_0} = \frac{n_a z_a + n_b z_b}{z_0} = \frac{n_a + n_b}{1} = N. \qquad (6)$$

Then
$$\left.\begin{aligned} n_a x_a + n_b x_b &= (n_a + n_b)\, x_0 \\ n_a y_a + n_b y_b &= (n_a + n_b)\, y_0 \\ n_a y_a + n_b z_b &= (n_a + n_b)\, z_0 \end{aligned}\right\} \qquad (7)$$

or
$$\left.\begin{aligned} x_0 &= \frac{n_a x_a + n_b x_b}{n_a + n_b} \\ y_0 &= \frac{n_a y_a + n_b y_b}{n_a + n_b} \\ z_0 &= \frac{n_a z_a + n_b z_b}{n_a + n_b} \end{aligned}\right\} \qquad (8)$$

And the equation of the straight line passing through the two ponits (x_a, y_a, z_a) and (x_b, y_b, z_b) is

$$\begin{vmatrix} x & y & z \\ x_a & y_a & z_a \\ x_b & y_b & z_b \end{vmatrix} = 0. \qquad (9)$$

If we put the values of x_0, y_0 and z_0 in eq. (8) for x, y and z of the above equation, we have

$$\begin{vmatrix} n_a x_a + n_b x_b & n_a y_a + n_b y_b & n_a z_a + n_b z_b \\ x_a & y_a & z_a \\ x_b & y_b & z_b \end{vmatrix} = 0.$$

This equation holds evidently, therefore the point (x_0, y_0, z_0) is on the straight line passing through the two points $(x_a\, y_a\, z_a)$ and (x_b, y_b, z_b).

Now let the thermodynamical potential of the solution Q be Φ_a, and that of R be Φ_b, then the total potential of the whole system is

$$\Phi = \Phi_a + \Phi_b.$$

When these two saturated solutions are in equilibrium, the change of the potential for the change dn_a and dn_b must be zero, viz.

$$d(\Phi_a + \Phi_b) = 0. \qquad (10)$$

Taking this equation together with eq. (7) and solving this differential equation, we have

$$\left.\begin{aligned} x_a &= f_a(x_0, y_0, z_0) & x_b &= f_b(x_0, y_0, x_0) \\ y_a &= \varphi_a(x_0, y_0, z_0) & y_b &= \varphi_b(x_0, y_0, z_0) \\ z_a &= \chi_a(x_0, y_0, z_0) & z_b &= \chi_b(x_0, y_0, z_0) \end{aligned}\right\} \qquad (11)$$

Eliminating x_0, y_0, z_0, we get

$$\left.\begin{aligned} g_a(x_a, y_a, z_a) &= 0 \\ g_b(x_b, y_b, z_b) &= 0 \end{aligned}\right\} \qquad (12)$$

These equations must correspond to Bancroft's formula

$$\left.\begin{aligned} \frac{x^{n_1} y}{z^{n+1}} &= C_1 \\ \frac{x^{n_2} y}{z^{n+1}} &= C_2 \end{aligned}\right\}$$

To determine the functional form of eq. (12), we must have knowledge of the functional form of eq. (10). Planck[1] gives the formula for the potential of any solution of solid or liquid state from the Nernst's heat theorem, as

$$\Phi = \int_0^T \frac{C_p}{T}\,dT - R\Sigma n_1 \ln c_1 - \frac{W}{T} \qquad (13)$$

where C_p is the heat capacity of the system, n_1 the number of molecules, c_1 the concentration, W the heat function represented by $W = U + pV$. Then we get the molecular potential of each component,

$$\frac{\partial \Phi}{\partial n_1} = \int_0^T \frac{\partial w_1}{\partial T}\frac{dT}{T} - \frac{w}{T} - R \ln c_1 \qquad (14)$$

because if we put $\frac{\partial W}{\partial n_1} = w_1$, $\frac{\partial W}{\partial n_2} = w_2$, ... then

$$\frac{\partial C_p}{\partial n_1} = \frac{\partial w_1}{\partial T}, \quad \frac{\partial C_p}{\partial n_2} = \frac{\partial w_2}{\partial T}, \ldots$$

If these two liquid phases are in equilibrium, the molecular potentials of each components in both phases must be respectively equal, viz.

$$\phi_A^{(a)} = \phi_A^{(b)}, \quad \phi_B^{(a)} = \phi_B^{(b)}, \quad \phi_S^{(a)} = \phi_S^{(b)}$$

where $\phi_A^{(a)}$ is the molecular potential of A in the first phase and $\phi_A^{(b)}$ is that of the second phase and so on. Representing every quantity in both phases similarly, we get from eq. (14)

$$\int_0^T \frac{\partial w_A^{(a)}}{\partial T}\frac{dT}{T} - \frac{w_A^{(a)}}{T} - R \ln c_A^{(a)} = \int_0^T \frac{\partial w_A^{(b)}}{\partial T}\frac{dT}{T} - \frac{w_A^{(b)}}{T} - R \ln c_A^{(b)}. \qquad (15)$$

In dilute solution w is a function of T and p only and in the any iosthermal change under a constant pressure, the expression $\int_0^T \frac{\partial w}{\partial T}\frac{dT}{T} - \frac{w}{T}$ remains constant; but in our case w is a function not only of p and T, but also of c. If the variation of concentration, however, be very small, we may take w to be independent of c and write eq. (15) as follows:

1 See Planck, Thermodynamik, 3 Aufl. § 291 and § 293.

$$\int_0^T \frac{\partial w_A^{(a)}}{\partial T}\frac{dT}{T} - \int_0^T \frac{\partial w_A^{(b)}}{\partial T}\frac{dT}{T} - \frac{w_A^{(a)}}{T} + \frac{w_A^{(b)}}{T} = R\ln\frac{c_A^{(a)}}{c_A^{(b)}} = K_A.$$

Since $c_A^{(a)} = x_a$, $c_A^{(b)} = x_b$, it foilows

$$K_A = R\ln\frac{x_a}{x_b}$$

or

$$e^{\frac{K_a}{R}} = \frac{x_a}{x_b}. \qquad (16)$$

Eliminating x_b by means of (7)

$$e^{\frac{K_A}{R}}\frac{n_a+n_b}{n_b}x_0 = x_a\left(1+\frac{n_a}{n_b}e^{\frac{K_A}{R}}\right).$$

In an analogous way, concerning the components A and B we have

$$e^{\frac{K_B}{R}}\frac{n_a+n_b}{n_b}y_0 = y_a\left(1+\frac{n_a}{n_b}e^{\frac{K_B}{R}}\right),$$

$$e^{\frac{K_S}{R}}\frac{n_a+n_b}{n_b}z_0 = z_a\left(1+\frac{n_a}{n_b}e^{\frac{K_S}{R}}\right).$$

Consequently, by combining above relations with $x_0+y_0+z_0 = 1$, it follows :

$$\frac{x_a}{e^{\frac{K_A}{R}}} + \frac{y_a}{e^{\frac{K_B}{R}}} + \frac{z_a}{e^{\frac{K_S}{R}}} = 1. \qquad (17)$$

Similarly we have

$$\frac{x_b}{e^{\frac{K_A}{R}}} + \frac{y_b}{e^{\frac{K_B}{R}}} + \frac{z_b}{e^{\frac{K_S}{R}}} = 1. \qquad (17_1)$$

Equations (17) and (17_1) are the relations corresponding to eq. (12); but it is a limiting case when the curves (5) or (12) may be seen as straight lines; in relating K_A, K_B, K_S are functions of x_a, y_a, z_a, x_b, y_b, z_b and envelopes of the straight lines (17) and (17_1) are the real solutions.

The point of intersection of the curves ak and kb or the critical saturated point k is a point where K_A, K_B, and K_S are all equal to zero.

Moreover, to establish the relation between conjugate points P and Q, or the compositions of two liquid phases in equilibrium, the following operation is appreciable.

Put the values of x_a, y_a, z_a, x_b, y_b, z_b in (11) to eq, (9) and eliminate two in x_0, y_0, z_0 for example y_0 and z_0, with the relation (7), then we have a relation

$$h(x, y, z, x_0) = 0. \qquad (18)$$

This is a relation having one parameter; and, differentiating with x_0, we get an envelope of straight line QR, viz.,

$$\left.\begin{aligned} h(x, y, z, x_0) &= 0 \\ \frac{\partial h}{\partial x_0} &= 0 \end{aligned}\right\} \qquad (19)$$

This is represented in the figure by the curve *lmn*. When we know the functions (12) and (19), the problem of the equilibrium of the three components system, where two liquid phases co-exist, is completely solved for a definite temperature and pressure. The curve *akb* or eq. (12) must be called an "equilibrium curve": and the envelope *lmn* or eq. (19) a "conjugate curve." To know the eqilibrium condition of any mixture of these three components, draw a tangent to the envelope from the point P representing the total mixture, then two intersecting points Q and R of the tangent with the curves of equilibrium are the points of the equilibrium.

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On Chemical Resistance.

By

Shinkichi Horiba.

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It seems quite reasonable to choose the velocity of a reacting system as the measure of the affinity of that system; but this is a merely superficial observation, because the velocity of a reacting system is not only a function of chemical affinity, but of temperature, pressure, light, catalyser etc. For instance, notwithstanding the great affinity of the detonating gas mixture of hydrogen and oxygen, its reacting velocity at room temperature is so slight that its practical measurement is impossible. Thus we have a very interesting problem concering the relation between the chemical affinity of a system and its velocity of reaction. Nernst[1] introduced the term *chemical resistance* with a definite meaning to express the relation.

The author here represents a study on the amount of chemical resistance and its signification.

Definition of Chemical Resistance.

As an expression of a reaction we will use the following:

$$\nu_1 A_1 + \nu_2 A_2 + \ldots\ldots \rightleftarrows \nu'_1 A'_1 + \nu'_2 A'_2 + \ldots\ldots \qquad (1)$$

where $A_1, A_2, \ldots A'_1, A'_2, \ldots$ are reacting substances and $\nu_1, \nu_2, \ldots \nu'_1, \nu'_2, \ldots$ their molecular coefficients. The reaction must proceed in such a manner that the free energy of the system shall diminish as required by the second law of thermodynamics, and the rate of diminution of the free energy be controlled by the resistance of the reacting system against the work done by this reaction. Nernst has expressed this reaction in a form analogous to the Ohm's law in electricity, namely

1 Theoretische Chemie, 7. Anfl., p. 705 (1913).

$$\text{Chemical resistance} = \frac{\text{Chemical force}}{\text{Velocity}}$$

or

$$\frac{dx}{dt} = \frac{F}{\mathfrak{R}} \qquad (2)$$

where $\frac{dx}{dt}$ is the velocity of the reaction and x the number of gram-equivalents per litre transformed during the reaction. F and $\mathfrak{R}$ designate the chemical force and resistance respectively. Let E be the free energy of this system, then $-\frac{dE}{dx}$ is the rate of diminution of the free energy during the reaction, namely chemical force or, in other words, a true expression of chemical affinity at that instant. Thus we have the following relation:

$$\text{Chemical resistance} = \frac{\text{Affinity}}{\text{Velocity}}.$$

Calculation of Affinity.

We can not determine the absolute amount of free energy of any system, but only estimate its diminution, namely the maximum work done, from the concentrations of reacting substances at the initial state of the system and those of the final state. If A designate the maximum work done by this system to establish the equilibrium, then

$$-\frac{dE}{dx} = \frac{dA}{dx} \qquad (3)$$

It has been shown by van't Hoff that the maximum work done during the reaction (1) will be expressed by

$$\mathfrak{A} = RT \ln \frac{C_1^{\nu_1} C_2^{\nu_2} \cdots\cdots}{C_1'^{\nu_1'} C_2'^{\nu_2'} \cdots\cdots} + RT \ln K \qquad (4)$$

where $\mathfrak{A}$ is maximum work and C_1, C_2, ... are the concentrations of the reacting substances before the reaction. K stands for $K = \frac{c_1'^{\nu_1'} c_2'^{\nu_2'} \cdots\cdots}{c_1^{\nu_1} c_2^{\nu_2} \cdots\cdots}$, $c_1, c_2, \ldots$ being the concentrations when the equilibrium was attained, and is the equilibrium constant. But it must be noted that the above formula of maximum work does not express the real maximum work done by the actual reaction; it is only an expression of maximum work done when the reacting substances on the left side of the equa-

tion are completely transformed into those on the right side according to the scheme of the equation, all substances maintaining their initial concentrations during the reaction.

Now we will calculate the maximum work for a more actual case, that is, the work done during the progress of the reaction towards the equilibrium in a gaseous system, or in a dilute solution, where simple gas laws are applicable. If we denote the initial state and the final or equilibrium state of the reaction by (I) and (II), and their free energies by F_1 and F_2 respectively, we have.

$$A = F_{\mathrm{I}} - F_{\mathrm{II}}.$$

Now $$F = U - TS, \qquad \Phi = S - \frac{U+pV}{T}$$

where U is the total energy of this system, S entropy and Φ thermodynamlcal potential.

Then $$T\Phi = TS - U - pV = -F - pV,$$

therefore $$F = -pV - T\Phi = -(R+\Phi)\,T$$

and we have $$A = F_{\mathrm{I}} - F_{\mathrm{II}} = -(R+\Phi_{\mathrm{I}})T + (R+\Phi_{\mathrm{II}})T = T(\Phi_{\mathrm{II}} - \Phi_{\mathrm{I}}). \quad (5)$$

That is to say the maximnm work is equal to the product of the difference of the thermodynamical potential and the absolute temperature.

Let $\phi_1^{\mathrm{I}}, \phi_2^{\mathrm{I}}, \ldots$ be the molecular potential of the reacting substances in the initial state, and $\phi_1^{\mathrm{II}}, \phi_2^{\mathrm{II}}, \ldots$ be those in the equilibrium state, then

$$\left.\begin{aligned} \Phi_{\mathrm{I}} &= \Sigma n_1^{\mathrm{I}}\, \phi_1^{\mathrm{I}} = \Sigma n_1^{\mathrm{I}}\, (\bar{\phi}_1 - R\ln C_1) \\ \Phi_{\mathrm{II}} &= \Sigma n_1^{\mathrm{II}}\, \phi_1^{\mathrm{II}} = \Sigma n_1^{\mathrm{II}}\, (\bar{\phi}_1 - R\ln c_1) \end{aligned}\right\} \qquad (6)$$

where $n_1^{\mathrm{I}}, n_2^{\mathrm{I}}, \ldots$ and $C_1, C_2, \ldots$ are the numbers of mols and the concentration of $A_1, A_2, \ldots$ in the initial state, and $n_1^{\mathrm{II}}, n_2^{\mathrm{II}}, \ldots$ and $c_1, c_2, \ldots$ those in the final state respectively, and Σ in eq. (6) refers obviously to all substances partaking in the reaction on both sides of the equation. And $\bar{\phi}_1, \ldots$ are functions relating only to temperature and pressure, and independent of concentrations. If the reaction proceeded isothermally under a constant pressure, these functions would remain constant during the reaction. Now we may calculate A from eq. (6).

$$\Phi_{\mathrm{II}} - \Phi_{\mathrm{I}} = \Sigma n_1^{\mathrm{II}}(\bar{\phi}_1 - R\ln c_1) - \Sigma n_1^{\mathrm{I}}(\bar{\phi}_1 - R\ln C_1)$$

$$= \Sigma(n_1^{\mathrm{II}} - n_1^{\mathrm{I}})\phi_1 - \Sigma n_1^{\mathrm{II}}\, R\ln c_1 + \Sigma n_1^{\mathrm{I}} l R\ln C_1$$

Adding the terms $+\Sigma n_1^{\mathrm{I}} R\ln c_1 - \Sigma n_1^{\mathrm{I}} R\ln c_1$ to the above expression, it follows that

$$\Phi_{II}-\Phi_I = \Sigma(n_1^{II}-n_1^I)\bar{\phi}_1 - \Sigma(n_1^{II}-n_1^I)R\ln c_1 + R\Sigma n_1^I(\ln C_1 - \ln c_1). \quad (7)$$

If the system be in equilibrium

$$\Sigma(\bar{\phi}_1 - R\ln c_1)\nu_1 = 0$$

or
$$\nu_1 \ln c + \nu_2 \ln c_2 + \ldots\ldots = \frac{\nu_1\bar{\phi}_1 + \nu_2\bar{\phi}_2 + \ldots\ldots}{R} = \ln K \qquad (8)$$

where K is the equilibrium constant and to the molecular coefficients of substances on the right side of the reaction scheme (1) $\nu_1', \nu_2', \ldots\ldots$ negative sign are assigned.
From (8) it follows

$$\begin{aligned}\Phi_{II}-\Phi_I &= \frac{n_1^{II}-n_1^I}{\nu_1}\Sigma\nu_1\bar{\phi}_1 - \frac{n_1^{II}-n_1^I}{\nu_1}\Sigma R\nu_1\ln c_1 + R\Sigma\frac{n_1^I}{\nu_1}(\ln C_1^{\nu_1} - \ln c_1^{\nu_1}) \\ &= \frac{n_1^{II}-n_1^I}{\nu_1}R\ln K - \frac{n_1^{II}-n_1^I}{\nu_1}R\ln K + R\Sigma\frac{n_1}{\nu_1}(\ln C_1^{\nu_1} - \ln c_1^{\nu_1}) \\ &= R\Sigma\frac{n_1^I}{\nu_1}(\ln C_1^{\nu_1} - \ln c_1^{\nu_1}).\end{aligned}$$

The reason, that in the above expression, $\frac{n_1^{II}-n_1^I}{\nu}$ can be placed outside of Σ, is as follows: Let the change of number of mols of A_1, A_2, ... during the reaction be $dn_1, dn_2, \ldots\ldots$, then the relation $dn_1 : dn_2 \ldots = \nu_1 : \nu_2 \ldots$ always holds, and $n_1^{II}-n_1^I = -\int dn_1$, therefore $\frac{n_1^{II}-n_1^I}{\nu_1}, \ldots$ are all equal to one another.
Now we have

$$\begin{aligned}A = T(\Phi_{II}-\Phi_I) &= RT\Sigma\frac{n_1^I}{\nu_1}(\ln C_1^{\nu_1} - \ln c_1^{\nu_1}) \\ &= RT\Sigma n_1^I(\ln C_1 - \ln c_1). \qquad (9)\end{aligned}$$

This is certainly the value of A in the expression $-\frac{dE}{dx} = \frac{dA}{dx}$, which express the affinity at any instant during the reaction. Now by means of equation (9) we will elucidate the method of calculation of the maximum work $\mathfrak{A}$, found in van't Hoff's expression. For simplicity, the following reaction will be taken

$$A + 2B \rightleftarrows C + 2D$$

when one mol of A and two mols of B act, the maximum work A_a is given by (9) as follows:

$$A_a = RT\,\Sigma\frac{n_1^{\mathrm{I}}}{\nu_1}(\ln C_1^{\nu_1} - \ln c_1^{\nu_1})$$

$$= RT\frac{\mathrm{I}}{\mathrm{I}}\ln C_A + RT\frac{2}{2}\ln C_B^2 - RT\frac{\mathrm{I}}{\mathrm{I}}\ln c_A - RT\frac{2}{2}\ln c_B^2$$

$$= RT\ln C_A C_B^2 - RT\ln c_A c_B^{2*}.$$

On the other hand, let the maximum work, when one mol of C and two mols of D act, be A_b, then we have similarly

$$A_b = RT\ln C_C C_D^2 - RT\ln c_C c_D^2.$$

And the difference $A_a - A_b$ is the maximum work done when one mol of A and two mols of B have transformed into one mol of C and two mols of D, that is

$$\mathfrak{A} = A_a - A_b = RT\ln C_A C_B^2 - RT\ln c_A c_B^2 - RT\ln C_C C_D^2 + RT\ln c_C c_D^2$$

$$= RT\ln\frac{C_A C_B^2}{C_C C_D^2} - RT\ln\frac{c_A c_B^2}{c_C c_D^2} = RT\ln\frac{C_A C_B^2}{C_C C_D^2} + RT\ln K.$$

Now we will calculate the expression for affinity $\frac{dA}{dx}$. When $\Sigma\nu_1$ is zero, that is, when during the reaction the total number of mols do dot change, or, in the case of dilute solution, when the number of mols transformed is negligible in composision with the total number of mols, we have

$$C_1 = \frac{n_1^{\mathrm{I}}}{N} \qquad n_1^{\mathrm{I}} = NC_1$$

where N is the total number of mols.

Then,
$$A = RTN\,\Sigma\,C_1(\ln C_1 - \ln c_1). \qquad (10)$$

The maximum work done when the concentration was diminished by x equivalents :

$$A_{-x} = RTN\,\Sigma\,(C_1 - \nu_1 x)\,\{\ln(C_1 - \nu_1 x) - \ln c_1\}.$$

Thus, chemical force or chemical affinity is

$$F = \frac{dA}{dx} = \frac{d[RTN\,\Sigma\,(C_1 - \nu_1 x)\{\ln(C_1 - \nu_1 x) - \ln c_1\}]}{dx}$$

where
$$\frac{d\{(C_1 - \nu_1 x)\ln(C_1 - \nu_1 x)\}}{dx} = -\nu_1(\ln(C_1 - \nu_1 x) + 1),$$

* The limiting values of $n_C \ln C_C, n_D \ln C_D$ when $x=0$ are equal to zero.

$$\frac{d\{(C_1-\nu_1 x)\ln c_1\}}{dx} = -\nu_1 \ln c_1.$$

Therefore we have $\frac{dA}{dx} = RTN\{-\Sigma \ln (C_1-\nu_1 x)^{\nu_1} - \Sigma\nu_1 + \Sigma \ln c_1^{\nu_1}\}$

$$= RTN\{\Sigma \ln (C_1-\nu_1 x)^{-\nu_1} + \Sigma \ln c_1^{\nu_1}\}. \qquad (11)$$

But, when during reaction some change takes place in the number of mols in the system, $\Sigma\nu_1$ is not equal to zero. In such a case let number of mols of the initial system be N and the change in the number of mols when the concentration is diminished by x equivalents,

$$N = n_1+n_2+\ldots\ldots+n_1'+n_2'+\ldots\ldots$$

$$\Delta N = (n_{1,x}-n_1)+(n_{2,x}-n_2)+\ldots+(n'_{1,x}-n'_1)+(n'_{2,x}-n'_2)+\ldots$$

where $n_{1,x}$, $n_{2,x}$, ... are the numbers of mols A_1, A_2, ... after the said change in the concentration.

Putting $n_{1,x}-n_1 = \Delta n_1$, $n_{2,x}-n_2 = \Delta n_2$, ...

we have $\Delta N = \Sigma \Delta n_1 = \Sigma \frac{\Delta n_1}{\nu_1}\nu_1 = \frac{\Delta n_1}{\nu_1}\Sigma\nu_1.$

As formerly stated, $\frac{\Delta n}{\nu}$ is identical for all substances, and putting $\frac{\Delta n}{\nu} = \alpha$, we get

$$\Delta N = \alpha\Sigma\nu_1.$$

Let $C_{1,x}$, $C_{2,x}$, ... be the concentrations after the said change in the concentration, then

$$C_{1,x} = \frac{n_{1,x}}{N+\Delta N} = \frac{n_1+\Delta n_1}{N+\Delta N} = \frac{n_1}{N+\Delta N} + \frac{\Delta n_1}{N+\Delta N}$$

$$= \frac{\frac{n_1}{N}}{1+\frac{\Delta N}{N}} + \frac{\nu_1\Delta n_1}{\nu_1(N+\Delta N)} = \frac{C_1}{1+\frac{\Delta N}{N}} - \nu_1 x.$$

Again $C_1 = \frac{n_1}{N}$, $x = \frac{-\Delta n_1}{\nu_1(N+\Delta N)}$

Therefore $x = \frac{-\Delta n_1}{\nu_1(N+\Delta N)} = -\alpha\frac{1}{(N+\Delta N)} = -\frac{\Delta N}{\Sigma\nu_1}\frac{1}{N+\Delta N}$

or $$\Delta N = \frac{-Nx\Sigma\nu_1}{1+x\Sigma\nu_1}.$$

The maximum work, when the concentration is diminished by x equivalents,

$$A_{-x} = RT(N+\Delta N)\,\Sigma\, C_{1,x}\{\ln C_{1,x} - \ln c_1\}$$
$$= RNT\left(\frac{1}{1+x\Sigma\nu_1}\right)\Sigma\{C_1(1+x\Sigma\nu_1)-\nu_1 x\}[\ln\{C_1(1+x\Sigma\nu_1)-\nu_1 x\} - ln\, c_1]. \quad (12)$$

The above expression is easily differentiable by x, viz.

$$\frac{dA}{dx} = RTN\left(\frac{1}{1+x\Sigma\nu_1}\right)\sum(C_1\Sigma\nu_1-\nu_1)[\ln\{C_1(1+x\Sigma\nu_1)-\nu_1 x\} - \ln\, c_1 + 1]$$
$$+ RTN\frac{\Sigma\nu_1}{(1+x\Sigma\nu_1)^2}\sum\{C_1(1+x\Sigma\nu_1)-\nu_1 x\}[\ln\{C_1(1+x\Sigma\nu_1)-c_1 x\} - ln\, c_1]. \quad (13)$$

Calculation of Chemical Resistance.

From the definition of (2) the chemical resistance is expressed as

$$\Re = \frac{-\frac{dE}{dx}}{\frac{dx}{dt}} = \frac{\frac{dA}{dx}}{\frac{dx}{dt}}.$$

For the expression of affinity $\frac{dA}{dx}$, the value of (13) in a general case or the value of (11) in the case of $\Sigma\nu_1 = 0$ or at reactions in dilute solutions, may be used. The expression of chemical velocity $\frac{dx}{dt}$ is represented in general as follows:

$$\frac{dx}{dt} = k_1\{C_1(1+x\Sigma\nu_1)-\nu_1 x\}^{\nu_1}\{C_2(1+x\Sigma\nu_2)-\nu_2 x\}^{\nu_2}.....$$
$$-k_2\{C_1'(1+x\Sigma\nu_1')-\nu_1' x\}^{-\nu_1'}\{C_2'(1+x\Sigma\nu_2')-\nu_2' x\}^{-\nu_2'}.....$$

when $\Sigma\nu' = 0$ or the reaction occurs in a dilute solution, this expression becomes more simple.

$$\frac{dx}{dt} = k_1(C_1-\nu_1 x)^{\nu_1}(C_2-\nu_2 x)^{\nu_2}\ldots\ldots - k_1(C_1'-\nu_1' x)^{-\nu_1'}(C_2'-\nu_2' x)^{-\nu_2'}\ldots\ldots$$

where k_1 is the velocity constant for the change from left to right in the reaction scheme and k_2 that of the opposite reaction. Moreover we have the relation $\frac{k_1}{k_2} = K$, when K is the equilibrium constant.

As one example of calculation of the chemical resistance, we will take the following reaction scheme:

$$A+2B \rightleftarrows C+2D.$$

Let the initial concentrations of A, B, C, D be a, b, c, d, and those of the final equilibrium state $(a-\xi), (b-2\xi), c+\xi), (d+2\xi)$, then from (11) the affinity of this reaction is

$$F = \frac{dA}{dx} = RTN\ln\frac{(c+x)(d+2x)^2}{(a-x)(b-2x)^2} + RTN\ln\frac{(a-\xi)(b-2\xi)^2}{(c+\xi)(d+2\xi)^2}$$

$$= RTN\ln\frac{(c+x)(d+2x)^2}{(a-x)(b-2x)^2} - RTN\ln K.$$

Therefore

$$\Re = \frac{\frac{dA}{dx}}{\frac{dx}{dt}} = \frac{RTN\ln\frac{(c+x)(d+2x)^2}{(a-x)(b-2x)^2} - RTN\ln K}{k_1(a-x)(b-2x)^2 - k_2(c+x)(d+2x)^2} \cdot (14)$$

This expression represents the chemical resistance as a function of x, and we can calculate it for all values of x from $x=0$ to $x=\xi$. At the limiting case, however, were $x=\xi$ and consequently $\Re=\frac{0}{0}$, it is indeterminate, but after the usual method, we get for it the following

$$\lim_{x=\xi}\Re = \frac{RTN\frac{4ABCD(B+D)+BD(ABD+CBD)}{AB^2CD^2}}{-k_1B(B+4A)-k_2D(D+4C)}$$

where $A, B, C. D$ denote $(a-2x), (b+x), (c-x), (d+2x)$ respectively, and this limiting value is definite.

Signification of Chemical Resistance.

In the preceeding sections the calculation of chemical resistance according to the principle of thermodynamics had been considered.

Now we are in a position to examine the signification of chemical resistance and for this purpose must make use of the idea of atom and molecule.

If there are two substances, A and B, they attract each other by the universal force of attraction; but in certain cases, according to their nature, another kind of attraction, namely chemical affinity, may act between them. Z. Gruwitsch[1] distinguished these two kinds of attractive force in the following way:

I Physical attractive force:
- *a*) It is not specific;
- *b*) its sphere of action is not limited;
- *c*) its action on a given mass is independent of the existence of other masses;
- *d*) its action is not atomistic, that is, it acts as a whole all over the closed surface and not in singual rays.

II Chemical attractive force:
- *a*) It is specific;
- *b*) its sphere of action is limited, probably to an atomic distance;
- *c*) its action on a given mass is different; according as one part of the force has already been saturated by another substance, or not;
- *d*) its action is atomistic, that is, it expresses itself by leaps in a few singular rays.

Under the supposition that chemical affinity has the above mentioned character, we will now consider the following special case as an example:

$$2H_2 + O_2 \rightleftarrows 2H_2O.$$

According to the above consideration, H_2 and O_2 would at first dissociate, and then when they approach each other within the atomic distance, the affinity will begin to act. The amount of the affinity is dependent not only on the concentrations of H and O, but also on that of H_2O already formed, as described under (*c*). Let the characteristic constant of the affinity between H_2 and O_2 be $\varkappa$, then the actual amount of the affinity is a function of the concentrations H_2O, H and O which contains the characteristic constant $\varkappa$ viz.,

$$F = f(C_H, C_O, C_{H_2O}, \varkappa).$$

1 Zs. physik. Chem., 87, 331, (1914).

On the other hand from (11), we have

$$F = \frac{dA}{dx} = RTN\{\Sigma \ln (C_1 - \nu_1 x)^{-\nu_1} + \Sigma \ln c_1^{\nu_1}\}.$$

Here the value of (13) must have been used, but for the sake of simplicity we have taken the above expression. As seen from it, the first term is only a simple function of C_H, C_O and C_{H_2O} and does not contain the constant x, and so the second term must contain it, but in all reactions with the same initial concentrations the second term is independent of x and consequently of C_H, C_O and C_{H_2O}. Therefore the second term itself must be a constant, namely

$$x = \Sigma \ln c_1^{\nu_1}$$

This is nothing but the well known mass law.

If we consider the chemical affinity and the mechanism of a chemical reaction as above described, the signification of chemical resistance is then clear. It consists from two terms of different properties. In the above example, they are:

1. The resistance to the dissociation of the molecules, H_2 and O_2 to atoms.
2. The probability that H and O approach each other within atomic distance by their kinetic energies.

With our present knowledge about atoms and molecules, it is impossible to calculate chemical resistance in a direct way.

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